THERMAL OXIDATION OF TI6AL4V FOR BIO-IMPLEMENTATION

A Thesis

By

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CERTIFICATE

This is to certify that the thesis entitled, “Thermal oxidation of Ti6Al4V for bio-implementation” submitted by **Geetanjali Gautam** for the requirements for the award of Bachelor of Technology in Biomedical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

Surface modification of Ti6Al4V was studied by thermally oxidizing the sample at temperature 750°C for 12,24 and 36 hrs of time duration for obtaining an oxide film possessing the properties of both anatase and rutile form. Phase characterization analyzed by XRD, morphological features assessed by SEM and the bio-activity of the surface of thermal oxidation treated and untreated samples through in-vitro test by soaking the samples in HBSS(SBF) for 40hrs and 80 hrs and observing the results with the help of SEM. The measurement taken by XRD indicated the presence of anatase and rutile in samples treated for 12hrs and 24hrs. SEM observation reveals the nature of oxide that longer is the duration the higher is it's crystallinity and greater thickness (the thickness of 36 hr treated sample is almost twice the 24hr one) due to nucleation and agglomeration. The treated samples immersed in SBF shows better apatite formation than the untreated ones as observed by SEM images.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

Biomaterials are defined as materials of natural or artificial origin that are used to direct, appendage, replace or support the functions of damaged and/or diseased parts of biological system . There are lots of materials used in the bio- medicine for a wide range of applications ranging from whole replacement of hard or soft tissues (like bone plates, total joint replacement, dental implants, pins, intra-ocular lenses, etc.), augment diagnostic or supportive devices (such as pacemakers, catheters, heart valves, etc.). There have been enormous efforts put for the development of biomaterials till date. Since, the demand of bone replacement implants has increased the rate of research on the progress of biomaterials that have improved bone analogue mechanical and physical properties as well as good biocompatibility. These can be divided generally into metallic, polymeric, ceramic and composite systems. Metals have reproducible properties and fabrication, reliable and rather inexpensive.

Titanium and titanium alloys are among widely used as bio-implant materials, particularly for orthopedic and osteosynthetic applications due to their low density, excellent biocompatibility, corrosion resistance and mechanical properties[1,2,3,4] Ti6Al4V is by far the most commonly used Ti based alloy having wide range applications in the fields of aerospace, chemical industry, marine and biomedical devices because of their combination of properties in terms of high strength to weight ratio, exceptional resistance to corrosion, and excellent biocompatibility. This material has affinity for oxygen and forms a native layer of oxide when comes in contact with the biological environment. Oxide film helps in better osseo-integration. But the native oxide layer possesses low mechanical and biocompatibility property. To overcome these type of problems, a new alloy materials and surface modification of Ti6Al4V has been widely explored.

Adhering properties of cells and proteins of body system is dependent upon surface chemistry of the biomaterial. Several surface modification methods such as, chemical treatment (acid analkali treatment) [5-8], electrochemical treatment (anodic oxidation) [9], sol–gel [10], chemical vapour deposition [11], physical vapour deposition [12], plasma spray deposition [13], ion implantation [14], thermal oxidation [15], etc. have been worked to obtain the surface with desired properties without transforming the property of the material, particularly the mechanical property and corrosion resistance etc. rather enhancing its overall features. Oxide film of Ti6Al4V remains in two allotropic forms – anatase and rutile. Anatase possess low hardness and high wettability whereas rutile form own high hardness and low wettability and high biocompatibility is it's another important feature. Hence a suitable phase mixture of anatase and rutile is required on Ti6Al4V alloy for enhanced biological response of the alloy possessing properties of both anatase and rutile phases, So in the present study thermal oxidation of Ti6Al4V has carried at fixed temperature with different treatment time duration to observe the nature of oxide form on the surface.

2 LITERATURE REVIEW

2.1 Biomaterial

Any material of natural or synthetic origin that interfaces with living tissue and/or biological fluid and/or illicit desired biological response and used to repair or replace or augment diseased, damaged parts are known as biomaterials. Biocompatibility, the basic requisite for any biomaterial, entails the ability of the material to perform effectively producing the pertinent host response for the desired application. This field of biomaterials research is considered as an elating and challenging one. It is exciting because of its potential applications and necessity to enhance the quality of life. It is challenging because of the various complexities it faces when biomaterials deals with biological environments for maintaining or restoring tissue and organ function .Various medical devices made of biomaterials include hip replacements, vascular grafts, assist devices, prosthetic heart valves and the less common neurological prostheses and implanted drug delivery systems. Over the ages quite a few materials have been acknowledged for biomedical application. These can be classified generally into metallic, polymeric, ceramic and composite systems. Combinations within same class or between classes have been tried and can be tried again for achieving properties required for specific application. In the past few decades, increase in the utilization of self-operating machines, participation of many persons in sports, defense activities, increased interest in motorcycles and bicycles, and day-to-day increasing traffic, has resulted in enormous increase in the number of accidents. This has necessarily led people to opt for orthopedic implants for early and speedy recovery and resumption of their routine activities.

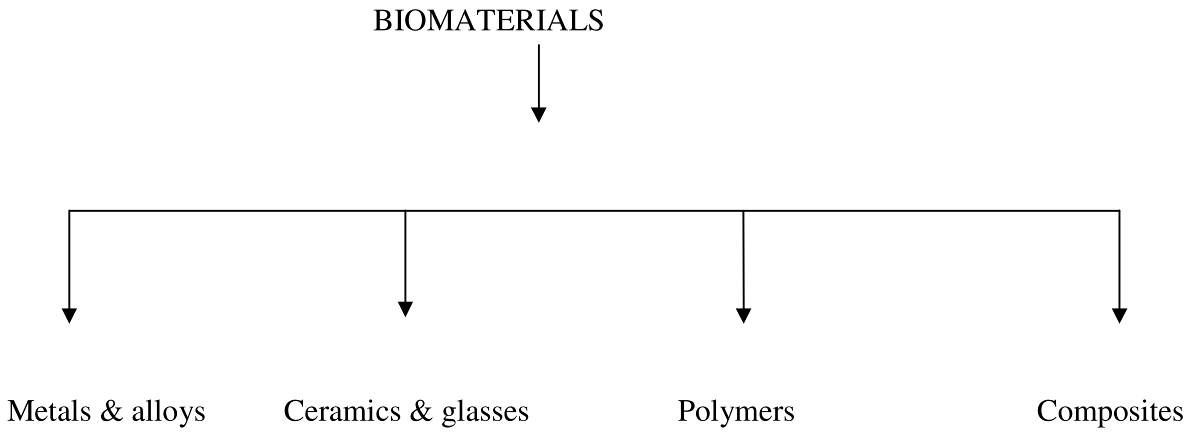

Table 2: Different Classes of Biomaterial and their Uses [1]

CLASS OF MATERIAL	CURRENT USES
Metal	
Stainless steel	Joint replacements, bone fracture fixation, heart valves, electrodes
Titanium and titanium alloys	Joint replacements, dental bridges and dental implants, coronary stents
Cobalt-chrome alloys	Joint replacements, bone fracture fixation
Gold	Dental fillings and crowns, electrodes
Silver	Pacemaker wires, suture materials, dental amalgams
Platinum	Electrodes, neural stimulation devices
Ceramics	
Aluminum oxides	Hip implants, dental implants, cochlear replacement
Zirconia	Hip implants
Calcium phosphate	Bone graft substitutes, surface coatings on total joint replacements, cell scaffolds
Calcium sulfate	Bone graft substitutes
Carbon	Heart valve coatings, orthopedic implants
Glass	Bone graft substitutes, fillers for dental materials
Polymers	
Nylon	Surgical sutures, gastrointestinal segments, tracheal tubes
Silicone rubber	Finger joints, artificial skin, breast implants, intraocular lenses, catheters
Polyester	Resorbable sutures, fracture fixation, cell scaffolds, skin wound coverings, drug delivery devices
Polyehtylene (PE)	Hip and knee implants, artificial tendons and ligaments, synthetic vascular grafts, dentures, and facial implants
Polymethylmethacrylate (PMMA)	Bone cement, intraocular lenses
Polyvinylchloride (PVC)	Tubing facial prostheses
Natural Materials	
Collagen and gelatin	Cosmetic surgery, wound dressings, tissue engineering, cell scaffold
Cellulose	Drug delivery
Chitin	Wound dressings, cell scaffold, drug delivery
Ceramics or demineralized ceramics	Bone graft substitute
Alginate	Drug delivery, cell encapsulation
Hyaluronic Acid	Postoperative adhesion prevention, ophthalmic and orthopedic lubricant, drug delivery, cell scaffold

Implant devices in general used in human body system to aid healing, correct deformities and restore the lost functions of the diseased or damaged part. As the implants are exposed to the dynamic biological environment of the human body, their design and structure dictated by anatomy and restricted by physiological conditions.

The purpose of synthesizing any bio-implant is to provide minimal physiological stress to the remaining body system so that the integrity and functionality of that specific part (say bone in case of orthopedic implant) and prosthetic materials are maintained over a long time period facilitating good service. Thus, materials suitable for implantation are those that are accepted by the body i.e. showing no undesirable effects and can withstand cyclic loading in the aggressive environment of the body.

2.2 Ceramics

Ceramics (for example: carbon, alumina, zirconia, bioactive glass and calcium phosphate)are inorganic compounds that have high compression strength and hardness, good wear and corrosion properties as well as chemically stable in the body environment. The use of ceramic materials limited due to their low tensile strength and fracture toughness. Their application in bulk form is thus limited to functions where only compressive loads are applied. There is reason for concern about the weak ceramic/metal bond and the integrity of this interface over a lengthy service-period under functional loading.

2.3 Polymers

Polymers (For example HDPE, PTFE, PLA, UHMWPE, PMMA, Polystyrene , etc.)are long chain molecules having low density, high damping capacity, produces low friction and extremely flexible considered for implant applications in various forms such as fibers , textiles, rods and viscous liquids. However, biochemical and mechanical factors of the body environment leads to degradation of polymers which results in ionic attack and forms hydroxyl ions and dissolved oxygen, leading to irritation of tissues and decrease in mechanical properties.

2.4 Composites

Composites are derived materials obtained by combining advantageous properties of metallic/ceramic/polymeric materials to achieve property which is higher than sum total of individual phase characteristics .Three distinct composite classes- Metal-Metal Composite, Polymer-Metal Composite and Ceramic-Metal Composite. It is essential that each component of the composite be biocompatible to avoid degradation between interfaces of the constituents.

2.5 Metals and alloys Metallic

Metals have reproducible properties and fabrication, reliable and rather inexpensive. They possess good stiffness and strength. Their processing can be done to get desired shape and fitting is also easy. Metallic implants are usually made of one of the three types of materials: austenitic stainless steels, cobalt–chromium alloys and titanium and its alloys (Sivakumar *et al* 1992, 1994).

Metallic biomaterials made from steel during early twentieth century turned out to be failures because of detrimental tissue reactions [17]. With the availability of 316 stainless steel post 1920 materials scientists found a material that was compatible with a biological environment [17]. Presently most of the artificial joints consist of a metallic component made from either alloys of titanium or CoCr. These are typically articulating against a polymer material like ultrahigh molecular weight polyethylene (UHMWPE). CrCo alloys have good wear resistance and due to the formation of stable chromium oxide, they are passive and corrosion resistant. They find application in metal on metal bearing surfaces for hip joints [17]. Titanium and its alloys due to their low density and a low strength to weight ratio are ideal for load bearing applications [16]. As a result of passive TiO2 that forms on the surface it provides a good solution for both orthopedic and dental applications.

2.6 Ti6Al4V

Ti6Al4V is known as the "workhorse" of the titanium industry as this is the by far the most commonly used Ti based alloy. This is an (alpha + beta) alloy which generally contain a combination of alpha and beta stabilizers and are heat treatable to various degrees; and beta alloys, which are metastable and contain sufficient beta stabilizers such as (Mo, V) to completely retain the beta phase upon quenching, and can be solution treated and aged to achieve significant increase in strength. Titanium and its alloys have a wide range of applications in the fields of aerospace, chemical industry, marine and biomedical devices because of their combination of properties in terms of high strength to weight ratio, exceptional resistance to corrosion, and excellent biocompatibility [18, 19]. The basic criterion for opting a metallic implant material is that it should possess the property of biocompatibility i.e. showing desirable local or systemic effects in the body and thus producing the most appropriate beneficial host response. The excellent biocompatibility is achieved by a dense TiO_2 layer that is always present in oxidizing media as in the human body fluid, and is rebuilt within milliseconds after any damaging [20]. Ti6Al4V applied in most of load bearing permanent implants because of their low density, good corrosion resistance, high fracture toughness and fatigue strength and low elastic modulus making it a good bone analogue material .The electrochemical features of integral and protective passivating oxide layer formed on the alloy during its long term stability in body environment plays a significant role for biocompatibility of implant. Many different types techniques for modifying surface modification have been created with the objective of improving the bonding at interfaces of the alloy and the bone

2.7 Surface Modification

Surfaces of commercial implants are found very complicated both with respect to their surface morphology and their chemistry. They are therefore not really suited to bridging the existing gap in our mechanistic understanding of the response of the biological (in vitro and in vivo) environment to the biomaterial surface. This, however, is important in order to design the type of surfaces which direct proper biological response in a particular cell/tissue situation, with the purpose of shortening healing time and minimizing toxic reaction to a 'natural level fostering the development of a particular biomaterial/cell architecture at the interface improving the mechanical properties, reliability, stability and long-term performance of the medical device [21]

Surface modification of materials for medical applications presents the possibility of combining the ideal bulk properties (e.g. tensile strength or stiffness for implants, electronic or optical properties for sensors) with the desired surface properties (e.g. biocompatibility or selectivity to a particular bio-molecule).

The goal is to exercise a degree of control over the way in which the body or individual bio-molecules respond to the material surface, whether this be bio-inertness, where the reaction to the surface is minimal bioactivity, where a particular response to an implant, such as the integration of a hip implant into the bone of the recipient, is desired, or selectivity, where the aim is the exclusive adsorption of a particular bio-molecule for sensing purposes. [22].

2.8 Surface Modification of Titanium and its Alloys:

The bulk properties of biomaterials such as biocompatibility, resistance to corrosion or controlled degradability, elastic modulus, fracture toughness and fatigue strength have been considered to be highly relevant during the time of the selection of the appropriate biomaterials for a specific biomedical application. The episodes after implantation comprise interactions between the biological fluid and artificial material surfaces, biological reactions, plus the particular response paths opted by the body. The material surface plays an extremely essential role in the response of the biological environment to the artificial medical devices. Another important reason for conducting surface modification to titanium medical devices is that specific surface properties that are different from those in the bulk are often required. For example, in order to accomplish biological integration, it is necessary to have good bone formability. In blood-contacting devices, such as artificial heart valves, blood compatibility is crucial. In other applications, good wear and corrosion resistance is also required. The proper surface modification techniques not only retain the excellent bulk attributes of titanium and its alloys, such as relatively low modulus, good fatigue strength, formability and machinability, but also improve specific surface properties required by different clinical applications.[24]

Titanium and titanium alloys are heat treated to achieve different properties, for example, to optimize special properties such as fracture toughness, fatigue strength, to increase strength, to produce an optimum combination of ductility, machinability and structural stability [23]. The tissue around a surgical implant is in contact with the surface oxide layer and not with the metal itself. **.** According to the different clinical needs, various surface modification schemes have been proposed and are shown below.

Laser-assisted surface treatments are used to change the microstructure of the surface layers of the materials (without changing the chemistry) via extraordinary high heating and cooling rates [25].

2.9 Compositional Modification

2.9.1 Oxidation

Over the past 40 years, many studies have been carried out on the oxidation of titanium [40-43], but less attention has been paid to the oxidation as a tribological surface thermochemical treatment of titanium alloys [28]. Oxidation of titanium and titanium alloys can be used to improve their tribological properties. Oxygen in solution with α-Ti produces significant strengthening of the material. The usually excellent corrosion resistance of titanium under normal conditions is largely due to the formation of very stable, highly adherent and protective oxide films on the surface.

2.9.2 Chemical methods

Chemical treatment of titanium and its alloys describes here include chemical treatment and electrochemical treatment (anodic oxidation) mainly based on chemical reactions occurring at the interface between titanium and a solution. The common ones are acid, alkali, H_2O_2, heat, and passivation treatments.

The oxide is predominantly TiO_2, but residues from the etching solution are frequently observed, particularly chemicals containing fluorine. It is also known that some treatments can lead to hydrogen incorporation in the surface region below the oxide [28]. These residues can remain even after post-thermal treatment of the etched surfaces. In addition, the acid treatment was often used to combine other treatment methods to improve the properties of titanium and its alloys. Wen et al. reported that the bioactivity of Ti alloy could be improved by two-step chemical treatments employing (HCl + H_2SO_4) and alkaline solution [29, 30].

Titania layers consisting of anatase and rutile are deposited on Ti substrates when soaked in a $TiOSO_4$ / H_2O_2 solution and aged in hot water. The corrosion of the Ti substrates by H_2O_2 and the hydrolysis of $TiOSO_4$ concertedly increased the supersaturation of Ti (IV), which favored the formation of thicker oxide layers. The aging in hot water promoted the precipitation of anatase and rutile in the surface layer, indicating that cleavage and recombination of the Ti–O–Ti bond took place. A large number of Ti–OH groups were rearranged and emerged accompanying the structural relaxation in the layer. Moreover, the aging in hot water enhanced the apatite-forming ability on the substrates in SBF. This was accounted for by the removal of residual impurities due to prior $TiOSO_4$ / H_2O_2 treatment. F. Xiao et al [31] found in vitro apatite deposition on titania film derived from chemical treatment of Ti substrates with an oxysulfate solution containing hydrogen peroxide at low temperature.

2.9.3 Electrochemical methods

Anodic oxidation encompasses electrode reactions in combination with electric field driven metal and oxygen ion diffusion leading to the formation of an oxide film on the anode surface. Anodic oxidation is a well-established method to produce different types of protective oxide films on metals. Different diluted acids (H_2SO_4, H_3PO_4, acetic acid and others) can be used as electrolytes in the process. Anodic oxidation can also be used to increase the oxide thickness to increase corrosion protection and decrease ion release, coloration, and porous coatings. The structural and chemical properties of the anodic oxides can be varied over quite a wide range by altering the process parameters, such as anode potential, electrolyte composition, temperature and current. A. Afshar et al [32] performed anodizing of titanium in phosphate-base solutions such as H_3PO_4, $NaH_2PO_4.2H_2O$ and Na_2HPO_4 at 9.75 mA /cm^2 and 35^{0}C under galvanostatic conditions. It is reported that the anodic films formed on Ti are compact and their thickness depends on the solution type and concentration. They observed that the major factor contributing to the decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current. Andrei Ghicov et al [33] reported that under specific sets of conditions highly self-organized titanium oxide nanotubes with significant amount of phosphorous species are formed with diameters varying from approx. 40 nm to 100 nm and length from approx. 100 nm to 4μm. J. Baszkiewicz et al [34] studied the modification of titanium surface by plasma electrolytic oxidation (PEO) and hydrothermal treatment. The oxide layers formed by PEO were porous, highly crystalline and enriched with Ca and P. After hydrothermal treatment, hydroxyapatite crystals precipitated on the surface. The results of electrochemical examinations show that the surface modification by PEO and hydrothermal treatment decreases the corrosion resistance of titanium.

In summary, anodization is a simple and effective method to modify the surface of titanium and its alloys for better biocompatibility and bioactivity. The anodic oxide film exhibits a variety of different properties that depend on the composition and microstructure of the materials and processing parameters, such as anode potential, electrolyte composition, temperature, and current.

2.9.4 Nitriding

Nitriding of titanium and titanium alloys has been investigated for many years and is used effectively for protection against wear. Nitrogen has a high solubility in Ti so it strengthens the surface layer significantly. Nitriding processes can cause the formation of a compound layer of TiN on top and Ti_2N beneath, with a hardness that can reach 3000 and 1500 HV, respectively [26]. Different values are given in Ref. [35], namely 1200 HV for $TiN_{0.6}$ and 1900 HV for $TiN_{0.97}$. Nitriding cannot be achieved in air because of the tendency for titanium to form TiO_2 in preference to either of the nitrides.

2.9.5 Gas nitriding

Gas nitriding is considered to be a promising method available for engineering applications because it can easily form a harder layer on the surface of the materials. The main advantage of gas nitriding is that it is independent of the geometry of the sample and does not require special equipment. A big disadvantage is that it requires high temperatures, 650–1000^{0}C, and a long time for nitriding, 1– 100 h, according to the literature. It is also well known that gas nitriding reduces the fatigue limit of titanium alloys [34]. The microhardness varies between 450 and 1800 HV for Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo.

2.9.6 Plasma nitriding

Plasma nitriding is a method for thermochemical treatment that has many advantages such as control of the phase formation and the depth of the nitrided layer. It requires short periods of nitriding time and it avoids oxidation. Different experiments have been performed at low temperatures from 400 to 950^{0}C for various periods of time from 15 min to 32 h. Micro-hardness values from 600 to 2000 HV for Ti–6Al–4Vand Ti–10V–2Fe–3Al and a compound layer with a thickness of about 50 µm have been obtained [35-43]. This type of treatment requires special equipment and high ionizing energy. One disadvantage of plasma nitriding is that it reduces the fatigue strength of titanium alloys; however, this problem can be overcome by reducing the processing temperature as reported by T. Bell, et al [46]. Nolan et al [47] reported wear behavior of TiN and TiN/Ti_2N thin films deposited by plasma nitriding processes, increased hardness/strength of the substrate and sliding wear behavior under all normal loads considered.

2.9.7 Ion Implantation

Ion implantation involves the bombardment of a solid material with a medium to high energy ionized atoms and offers the ability to alloy virtually any elemental species into the near surface region of any substrate. The advantage of such a process is that it produces improved surface properties without the limitation of the dimensional changes or delamination found in the conventional coating. A large number of reports have been published on the application of ion implantation, mainly nitrogen but also carbon or oxygen, to improve the wear resistance of titanium alloys [54, 55]. In particular the alloy Ti6A14V, due to its excellent combination of high strength, low density and high corrosion resistance, has been much studied by many researcher having in mind aeronautical and medical applications. There is a good agreement in that nitrogen, carbon or oxygen implantation of commercially pure a-titanium hcp and the α/β Ti6A14V alloy can produce more than a twofold hardness increase [56, 57]. Friction in this alloy is reduced significantly by ion implantation and wear resistance is markedly improved. The protective surface oxide layer formed on titanium and its alloys provides a useful low frictional behavior, but when this oxide is removed, a rapid adhesive wear occurs against many counteracting materials. An increase in surface hardness by ion implantation allows the material to resist plastic deformation at higher stresses and therefore provides a better support for the oxide during wear. Ion implantation of nitrogen or other ion species effectively protect the surface of Ti alloys during wear until the protective oxide layer wears away. Once that break-through of the oxide layer has been produced, wear on the Ti surface proceeds very rapidly as in the unimplanted material. This is characterized by formation of hard oxide particles that promote severe scratching by a three body abrasion mechanism when rubbing against a UHMWPE pin [56, 58]. In this instance, ion implantation increases the load bearing capacity of the surface and modifies the chemistry of the protective oxide layer, but when the latter is removed the wear mechanism is identical in both implanted and unimplanted surfaces.

Ion implantation, however, offers the possibility both of improving wear resistance and of improving, or at least not impairing, fatigue resistance [59-61]. Ion implantation with boron greatly increases the incubation period for measurable wear loss from Ti-6AI-4V; during this period the coefficient of friction remains at its initial low value. Qualitatively similar, but rather smaller, effects of boron, nitrogen and carbon ion implantation were also noted under relatively mild wear conditions (low contact stresses) [77].

2.9.8 Thermal Oxidation

Some researchers found the simplest method to increase the corrosive resistance of titanium by anodic oxidation . In an attempt to promote bone integration, blasting process in combination with acid etching on cpTi or Ti6Al4V alloy implant surfaces has been developed.

3. EXPERIMENTAL PROCEDURE

3.1 Synthesis

A Ti6Al4V sheet first cut into10 small rectangle shape samples. Samples were first grinded and then polished using various grades of SiC (1/0, 2/0,3/0 and 4/0) abrasive paper to give plane polished surface. After the paper polishing, the next step was cloth polishing followed by diamond polish by applying hiffin solution and diamond paste. This whole polishing procedure gives mirror finish to sample surfaces. Proper care is taken during polishing so that the extent of plastic deformation will be very less to cause any significant change in the oxidation kinetics/mechanism. Thermal oxidation was carried out in a muffle furnace at 750 °C for 12, 24 and 36 hours in air. The rate of heating was kept at 5 °C min^{-1} in all the experiments. After thermal oxidation treatment, the Ti6Al4V samples were allowed to cool in the furnace itself at its own cooling rate.

3.2 Phase Characterization

3.2.1 X-Ray Diffraction Analysis

The composition of the pure Ti6Al4V and thermally oxidized samples was analyzed using X-Ray diffraction. Samples were studied in a X'PERT PANalytical X-Ray diffractometer with a graphite monochromator. A Cu target was used as X-Ray source (CuK-radiation). A graphite monochromator was located in front of the proportional counter in order to reduce the background noise in the detector. X-Ray intensity was measured for angles in the range $20° < 2\Theta° < 80°$ with scan rate of 2° per minute. The diffraction patterns produced were then compared with the existing data using JCPDS data file. To identify the phases present, the location of peaks in the XRD profiles were compared to reference spectra.

3.3 Morphological Characterization

SEM Analysis

In this experiment scanning electron microscope (SEM) has been used thrice for analyzing three different aspects of surface of Ti alloy samples.

3.3.1 Oxide Morphology- The surface morphology of thermal oxidation treated Ti6Al4V alloy was assessed by scanning electron microscope**.**

3.3.2 Oxide Thickness- A closer examination of the surface morphology of the oxide layer formed at different temperatures and for various durations of time indicates the nature and thickness of the oxide film.

3.3.3 In-vitro bioactivity test using Hank's Balanced Salt Solution - Investigation of formation of apatite film after the in-vitro test of samples where both the heat treated and untreated samples absorbed in simulated body fluid(SBF) solution. In this experiment Hank's Balanced Salt Solution was used as SBF solution. The samples were kept in solution different time duration to observe apatite formation.SEM analysis was done for the purpose.

4. RESULTS AND DISCUSSIONS

4.1 Phase Characterization

4.1.1 X-Ray Diffraction Analysis

The influence of the crystallization temperature on the structure of the oxide produced by the thermal oxidation process was measured with XRD. Samples were examined to assess any reaction taking place between elements of thermally oxidized Ti6Al4V due to temperature effects. Obtained peaks were matched with JCPDS data card no. 75-1752(TiO_2), 44-1294(αTi) and card no. 44-1288(β Ti).

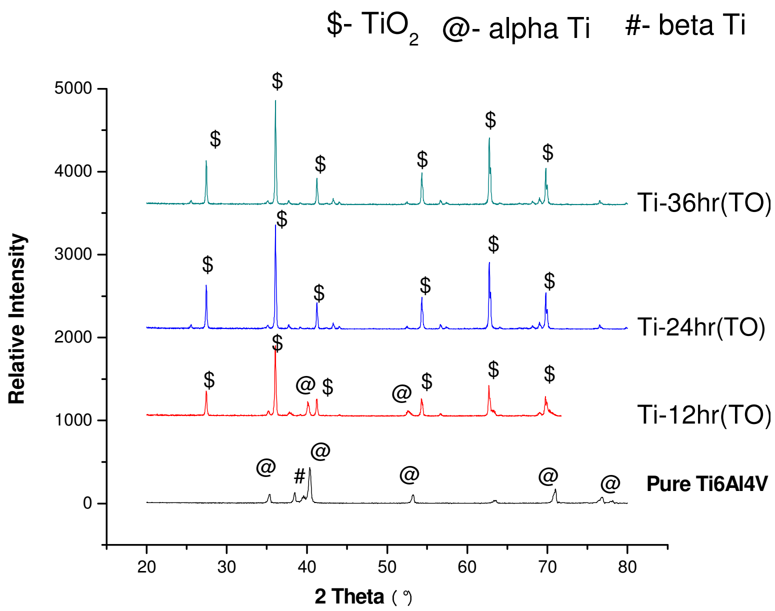

Fig 1 XRD pattern plotting of untreated and thermal oxidation treated Ti6Al4V for various durations of time in air.

The XRD patterns of untreated and TO Ti6Al4V alloy are represented in Fig. 1. Untreated Ti6Al4V alloy is comprised of α + β phase (denoted '@' as alpha Ti and '#' as beta Ti) in Fig. 1. The XRD patterns of thermally oxidized Ti6Al4V alloy display the presence of rutile as the predominant phase along with a small amount of α-Ti and α/β-Ti peaks.. However, with increase in treatment time from 12 to 36 h, the intensity of the anatase peaks reduces with a concurrent increase in Ti/Ti(O) peaks .Siva Rama Krishna et al.[48]have reported the formation of Ti(O) at temperatures less than 700°C and rutile at and above 800°C as the dominant phase following oxidation of titanium. Guleryuz and Cimenoglu[49]have reported the presence of anatase phase when the Ti6Al4V alloy was oxidized at 600 °C for 24 and 48 h whereas rutile was the only dominated phase when the alloy was oxidized at 650 °C for 48 h.

The presence of only the rutile phase on Ti6Al4V oxidized at 750°C for 8h suggests the formation of a thick oxide film. The presence of α-Ti and Ti(O) peaks at 500°C indicates the formation of a thin oxide film whereas the presence of α-Ti, Ti(O) and rutile at 650 °C points out that the thickness of the oxide layer would lie between those oxidized at 500°C and 800°C.

4.2 SEM Analysis

4.2.1 Oxide Morphology

The surface morphology of thermal oxidation treated Ti6Al4V alloy samples at temperature 750°C for different durations of time such as 12 hours, 24 hours and 36 hours examined by SEM noticeably shows the presence of oxide film over the treated surface.

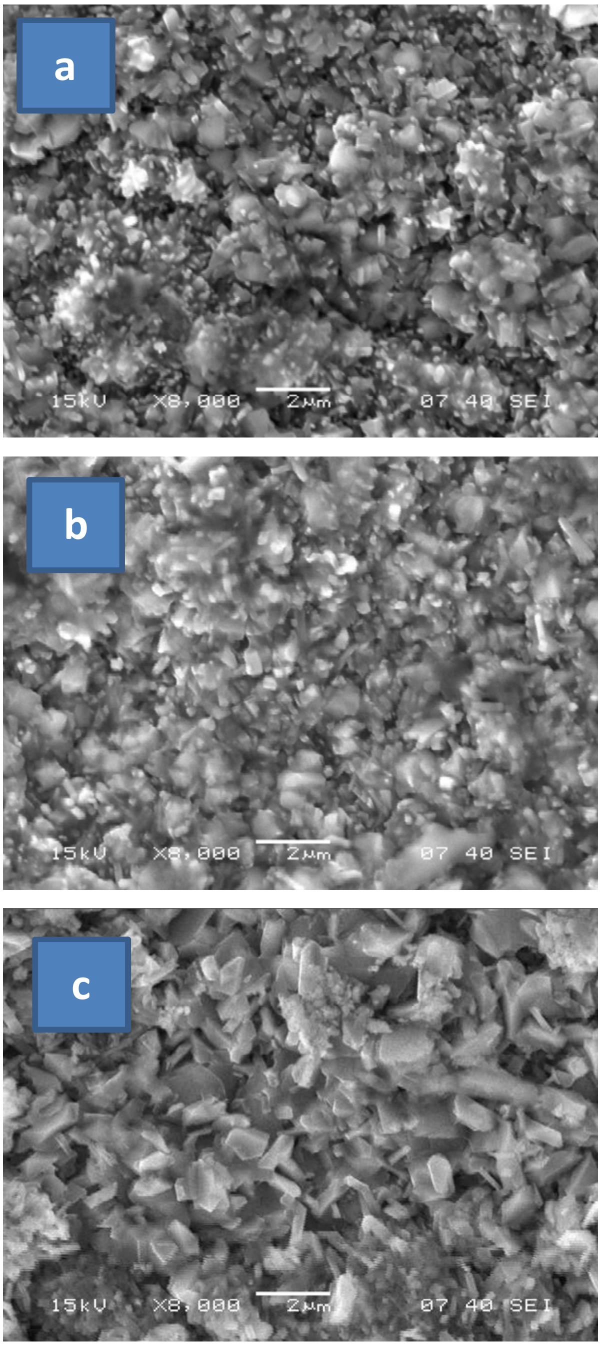

Fig2. SEM micrographs of oxides formation

(a) Thermally oxidized Ti6Al4V for 12 hrs.

(b) Thermally oxidized Ti6Al4V for 24 hrs.

(c) Thermally oxidized Ti6Al4V for 36 hrs.

A close visual observation of the surface morphology of the oxide film created at 750°C for various durations of time signifies the nature of the oxide layer. The surface morphology distinctly reveals the presence of a thick oxide scale without flaking or spallation throughout the surface. Agglomeration has been observed in all the three sample surfaces. The SEM picture (a) from Fig.2 shows initiation of formation of particle and in the second micrograph (b) the growth continues but the formation of particles is not uniform. On the other hand the third micrograph (c) thermally oxidized for longer duration indicates formation of crystal particles in a uniform fashion. This shows that the increase in treatment time from 12 to 36 hrs at 750°C affects the growth of particles, the oxide particles seem to grow outward and swathe the entire surface of the oxidized alloy. Nucleation and agglomeration displays increase in treatment time at 750 °C facilitates an increase in the size of the oxide particles, which leads to enlargement in gap between the nearby oxide grains or porosity of the oxide layer.

4.2.2 Oxide Thickness

Ti6Al4V responds immediately when comes in contact with oxygen and forms a TiO_2 layer on its surface. The oxide formation of titanium has been studied earlier on the surface that prevents it from further oxidation or oxygen diffusion at lower temperature. The occurrence of mainly the rutile phase on Ti6Al4V oxidized at 750 °C for 24hrs and 36 hrs suggests the formation of a thick oxide film.

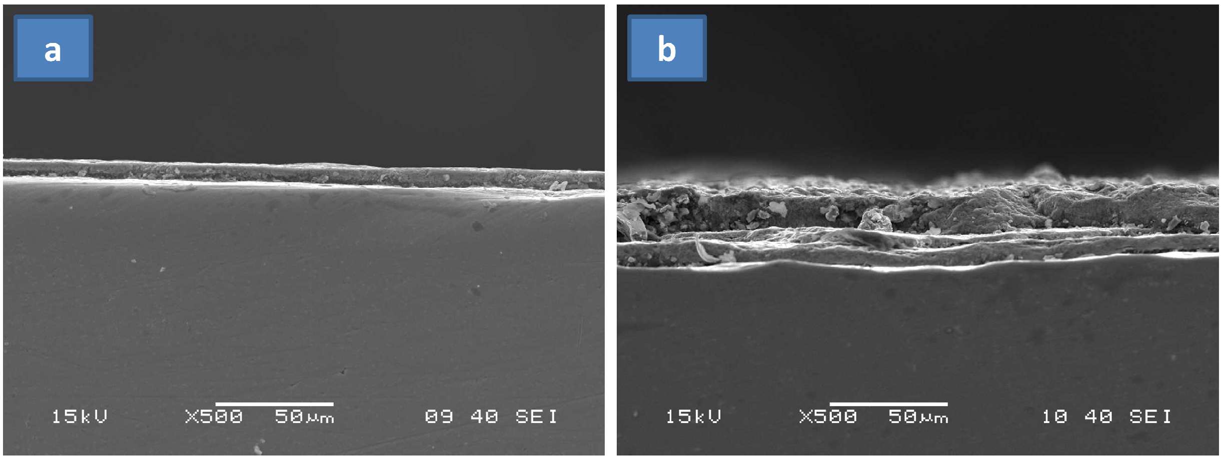

Fig3. SEM micrographs showing the thickness of the oxide formed at the surface of thermally oxidized at 750°C for (a) 24 hrs (b) 36 hrs.

At sufficiently high temperatures, oxygen diffuses through the oxide layer, and at the metal–oxide interface, it reacts with titanium to form TiO_2. Formation of an oxide layer is accompanied with the dissolution of diffusing oxygen in the metal beneath it. An increase in temperature accelerates the rate of oxidation, thus allowing the formation of a thicker oxide layer with a deeper oxygen diffusion zone. The oxidation of titanium and its alloys follows different rate laws as a function of temperature. Below 400 °C oxidation of titanium follows a logarithmic rate law whereas a transition from logarithmic to parabolic or an approximately cubic rate law is observed between 400 and 600 °C. The oxidation of titanium follows parabolic rate law between 600 and 700 °C while after extended reaction it transforms into an approximately linear rate [50,51]

Table 2: Calculated value of thickness of oxide layer

Duration Time(hrs)	**Oxide thickness(μm)**
24	10.50
36	20.30

Measurement of thickness of oxide film over the thermal oxidation treated for 24hrs and 36hrs was done and the obtained values were tabulated in table.1.This indicates that with increase in time duration the thickness of oxide film formed also increases.

4.2.3 In-vitro bioactivity test using Hank's Balanced Salt Solution

For testing the apatite-forming capacity of the thermal oxidation treated and untreated samples were immersed of Hank's balanced salt solution (SBF solution) in a glass beaker at pH 7.4 and 37 ° for 40hrs and 80hrs. After immersion both the heat treated and untreated samples were washed in distilled water and then air dried. SEM analysis was performed to evaluate the formation of apatite over the thermally oxidized and untreated samples over the immersion period of 40hrs and 80hrs respectivel

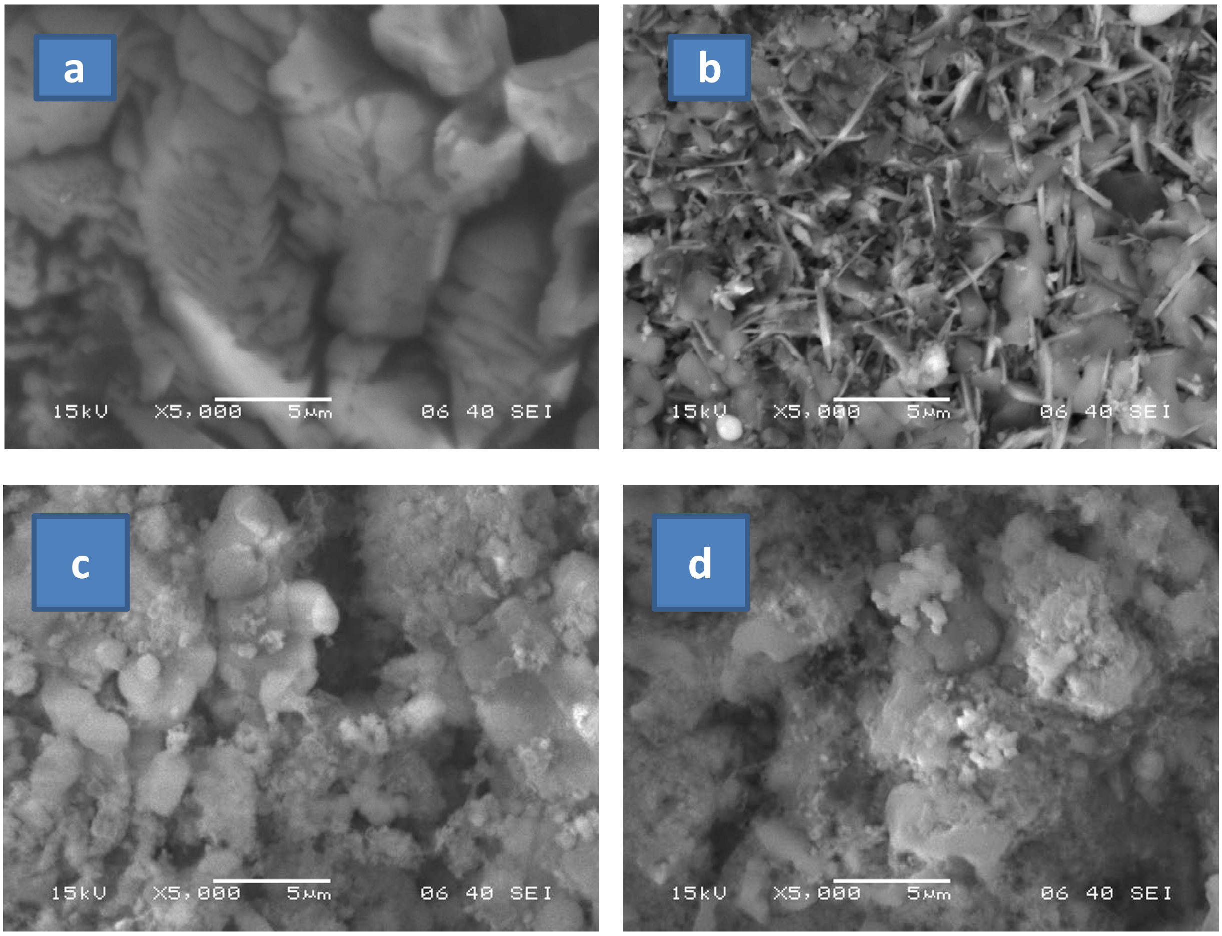

Fig4. SEM micrographs of apatite formation on thermal oxidation untreated and treated Ti6Al4V samples. (a) Untreated sample soaked in HBSS for 40hrs. (b) 24hrs treated sample soaked in HBSS for 80hrs. (c) Untreated sample soaked in HBSS for 80hrs. (d) 36hr treated sample soaked in HBSS for 40hrs.

The effect of thermal oxidation treatment of Ti6Al4V samples on apatite (calcium phosphate) formation was investigated in simulated body fluid (SBF) which simulates inorganic part of systemic circulation of human body .HBSS was used as SBF in this experiment. The SBF solution contains components like sodium chloride, potassium chloride, potassium phosphate, monobasic KH_2PO_4, Na salt ,sodium phosphate, dibasic Na_2HPO_4, anhyd magnesium sulfate, anhyd $MgSO_4$, calcium chloride and anhyd. sodium bicarbonate .The samples were exposed into SBF solution under static conditions in a biological thermostat at37°C.

In vitro test compares results of the untreated and treated samples in SBF solution forming apatite. Analysis confirmed that thermally oxidized samples (Fig. 4 b-d) had absorbed Ca^{2+} and $(PO_4)^{3-}$ ions immediately after immersion and points towards better apatite formation than the untreated samples(Fig. 4 a-c) . The pattern, thickness and quality of the hydroxyapatite formed on the samples vary on the basis of surface of treated/untreated samples and period of time of immersion in SBF. The apatite layer formed on treated and kept soaked in SBF for longer duration seems globular and homogeneous in nature. These statements can be verified by referring to the SEM images (Fig.4).

5. CONCLUSION

- Of the3 thermal oxidation treated Ti6Al4V samples, only the sample oxidized for 12 hrs shows presence of both anatase and rutile. This indicates that at 750°C if a sample oxidized for duration between 12-24 hr can reflect better results.
- Sample thermally oxidized for longer duration as observed by comparing the SEM images of samples treated Thickness of oxide of 36hr treated sample is almost twice the 24hr one. This indicates that with increase in time duration the thickness of oxide film formed also increases.
- The treated samples displays better apatite formation than the untreated samples indicating good bioactivity of heat treated samples.

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